Line intensities: the good, the bad and the ugly

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Abstract

Atmospheric remote sensing requires that line intensities be measured and modeled to 5% or better in laboratory studies. Successes and failures for analyses of carbon monoxide, methane, methanol and nitric acid will be reviewed.

Summary

The physical structures, chemical compositions, distribution of aerosols and cloud structure of planetary atmospheres can be determined through remote sensing by spectroscopic techniques. Databases of molecular line parameters are required as input for radiative transfer calculations in order to interpret the atmospheric spectra. The parameters needed are line center frequencies or positions and lower state transition energies as well as transition line intensities and line shape parameters as a function of temperature. The shape parameters are characterized by the Doppler widths, by the Lorentz widths when broadened by a foreign species, and for gases like CO_2, by the line mixing and far-wing coefficients. Typically, many thousands of ro-vibrational transitions contribute to the spectral signature of a particular molecule in each of its infrared active regions. Accuracies needed for these parameters vary according to the application. The requirements for planetary data in general are $\approx$ ½% for lower states, 5% for line intensities, 10% for half widths and 0.0003 to 0.5 cm^{-1} for line positions. The increasing sophistication in observing facilities often produces greater demand for better parameters, and some experiments to monitor the terrestrial atmosphere are now calling for some intensities to be known to 1%.

Our ability to provide accurate intensities from laboratory studies depends on how well we can measure the individual transitions and then apply quantum mechanics to reproduce the available measurements. The precision to which line intensities are obtained is affected by the quality of the spectrometers and the detectors, the signal to noise ratio, the ability to resolve individual transitions and the retrieval algorithms and procedures. Intensities of a simple diatomic like carbon monoxide can readily be measured in the infrared to 1% because the molecule gives rise to isolated ro-vibrational transitions which are relatively strong in a spectral interval covered by a good detector (InSb). Such precision is more difficult to achieve for methane in adjacent spectral regions simply because its transitions tend to arise close together in manifolds. The difficulty increases when many transitions are unresolved even at Doppler-limited resolution, such as is the case in the higher overtone regions of light species (methane) and heavy molecules (nitric acid) in general.

After good laboratory measurements of intensities are obtained, there must be successful applications of the appropriate Hamiltonian models and transitions moment expressions in order to provide a complete database of molecular line parameters. For the CO molecule, the expressions are simple and generally adequate, but for species such as water, methane, methanol and nitric acid, the degree of success varies greatly. The current status of intensities studies for these species and their representation in the public databases will be discussed and summarized. An example is given for methane.

STATUS OF METHANE MEASUREMENTS AND ANALYSES

REGION μm	POSITIONS Measured and Modeled	INTENSITIES Measured and Modeled
ROTAT.	G.S. 0.036 MHz combination differences in ν_4, ν_2 0.00006 cm^{-1}	*Need measurements*
5 - 10	ν_4, ν_2 0.00006 cm^{-1} 9 hot bands 0.002 cm^{-1}	1200 lines of ν_4, ν_2 ±3% rms 1700 lines ±5% rms
3 - 5	ν_3, ν_1, $2\nu_4$, $\nu_2+\nu_4$, $2\nu_2$ modeled C-12 to 0.0020 cm^{-1} C-13 to 0.0007 cm^{-1}	2400 lines measured modeled to 3% *Need hot bands measured/ modeled*
2.1 - 3	8 bands of C-12 0.0002 cm^{-1} measured vs 0.03 cm^{-1} rms modeled *no C-13 assignments* *need more analysis*	≈ 5000 lines measured to 2 -15% Modeled to 15% - 50% rms *Need more analyses*
1.5 - 2.1	14 bands with partial assignments to 8 bands including $4\nu_4$ and $\nu_1+\nu_3$ positions calc. to ~0.1 - 0.2 cm^{-1} *Need more analyses*	~3000 measured intensities selected lines modeled to 20%-60% rms *Need more analyses*
0.8 - 1.5	*Need more analyses*	*Need more analyses*

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